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An Analysis and Calculation of the Optical Thin Film Packing Density and Density Uniformity

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Abstract: The packing density of deposited optical thin films is usually calculated by the variation of index values in vacuum and in atmospheric humidity. In our IAD experiments, we found that the packing density of some films calculated by this method is larger than 1.0. This means its structure is denser than that of amorphous nature. The reason for this is it has a strong compressive stress in film. We also found that the wavelength shifts of some films deposited by IAD don't have a dependence upon the packing density because they have different microstructural uniformity under different process parameters. The packing density and density uniformity coefficient deposited by EB and IAD with different process parameters are calculated and analyzed. The microstructures of the film were investigated by means of SEM.

Key Words: Optical Thin Film, Packing Density, Density Uniformity, Microstructure.

光学薄膜的堆积密度及密度均匀性的分析与计算

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摘要: 光学薄膜的堆积密度通常是利用薄膜在真空及大气中折射率的变化来计算, 在 IAD 实验中, 我们发现有些薄膜的堆积密度大于 1.0, 这意味着薄膜的密度比自然界中的材料密度还要密积, 原因是薄膜具有较大的内压应力, 我们还发现了薄膜的波漂不依从于堆积密度。这是因为它们在不同的蒸发条件下具有不同的密度均匀性, 在用 EB 及不同条件的 IAD 的情况下, 我们计算并分析了堆积密度及密度均匀系数, 并用 SEM 观察了薄膜的微结构。

关键词: 光学薄膜, 堆积密度, 密度均匀性, 微结构。

1 Introduction

A water sorption phenomenon in optical coatings has been understood. The packing density of deposited optical coatings is greatly affected by the microstructure. Since ion-beam techniques were applied in optical coatings, a dense film can be obtained to improve the

environmental stability. To distinguish these properties, the packing density P is usually adopted[1,2]. The deposited optical thin film can be divide into two parts, one, the impenetrable skeleton (solid) part of the film consisting of the deposited film material, and the other the pore(void)part. Then, the packing density is defined as:

$$P = (volume\ of\ the\ solid\ part\ of\ the\ film)/(total\ volume\ of\ the\ film). \quad (1)$$

The theory and results of experiment show the following model: In the film growth during deposition without the ion-beam bombardment, small structural nuclei such as the nucleus for later growing dendrites are formed at first and then the voids appear in the films among these nuclei of appropriate size. During further film thickness growth, the structural units tend to cluster into larger groups. The voids in the group are closed, such that larger voids appear among the groups rather than the dendrites, and these groups of dendrites form the observed columns. In the film growth during deposition with the ion-beam bombardment, since bombardment of the energetic ion acts as the displacement effect and the promotion effect of migration for adherent atoms or molecules, the film microstructure will be improved, and the packing density will be higher.

However, the packing density calculated by equation (1) is difficult to solve. In case of the optical thin films ignoring the absorption, it is usually calculated by the film index in vacuum and in atmospheric humidity. In this experiment, we found that some films deposited by IAD are with a packing density larger than 1.0, and some do not show a dependence of wavelength shift upon packing density. These phenomena will be explained, and the new definitions of relative packing density and density uniformity will be introduced in this paper.

2 An Analysis and Calculation of the Optical Thin Film Packing Density

To obtain the value of the packing density, two methods have been introduced[1]. One is by a scanning spectrometer, and the other by a quartz crystal microbalance. The scanning spectrometer has been extensively in use recently. Some calculation models are described by Kinoshita and Nishibori[3] adopting a non-structural model where the film will be composed of the skeleton, i.e. solid part and voids, Chopra et al.[4], Bragg and Poppard[5], and respectively showing the following:

$$P = (n - n_v)/(n_b - n_v) \quad (2)$$

$$P = [(n_b^2 + 2)(n^2 - n_v^2)]/[(n^2 + 2)(n_b^2 - n_v^2)] \quad (3)$$

$$P = [(n_v^2 + n_b^2)(n^2 - n_v^2)]/[(n_b^2 - n_v^2)(n^2 + n_v^2)] \quad (4)$$

where n_b, n_v, and n are bulk, void, and film refractive index, respectively. In vacuum, $n_v = 1$ and n can be calculated utilizing the data obtained by a spectrometer. For the packing density, Various kinds of material by changing five different parameters were calculated by Ogura[1]. All the results of packing density are less than that of unity. However, in case of a process with the presence of energetic ions, there are some unsolved problems in equations (2)~(4). For example, in the IAD process with oxygen ion bombardment experiments, an index of amorphous SiO_2 film with excellent stoichiometry can be obtained at high values of about

1.476 at 550 nm than with the bulk index value of SiO_2, 1.460 at 550 nm, given by J. R. Pilipp[6]. Inserting the thin film index and bulk index of SiO_2 into equations (2)~(4) yields values of P at 1.035, 1.030, and 1.026, respectively. All the results of packing density are larger than unity. This phenomenon does not only appear in the case of SiO_2 film, but also in almost all dielectric films, particularly those obtained by ion-beam or plasma assisted deposition. A possible explanation is that the film is very dense with a larger internal compressive stress.

Another problem is how to determine the bulk index n for an amorphous material that does not exist in nature or never investigated before. For example, in the case of TiO_2 film, its bulk index is very difficult to determine. On the other hand, TiO_2 film is possible of the index values from 2.18 to 2.65 at the wavelength of 550nm deposited by various methods[7~9]. For calculating the packing density in this case, an arbitrary bulk index value is supposed and defined as the related bulk index. If setting the related bulk index value of TiO_2 to 2.50 or 2.70 at a wavelength of 550nm, the corresponding evaporated film indices are set at 2.180, 2.285, 2.365, and 2.650. In the case of the related bulk index value of 2.50 and using equation (4), the packing densities with respect to the above TiO_2 film indices are 0.9008, 0.9370, 0.9621, 0.9987, and 1.0367, respectively. The ratios of their packing densities are 0.8689: 0.9038: 0.9280: 0.9633: 1.0. In the case the bulk index value is 2.70, the packing densities of the above film indices are 0.8597, 0.8943, 0.9182, 0.9531, and 0.9894, respectively with ratios of 0.8689: 0.9038: 0.9280: 0.9633: 1.0. Thus, they yield the same ratios though they have different packing densities calculated by different bulk indices. The same results can be obtained by equations (2) and (3). Therefore, the packing density can be defined as relative packing density.

3 An Analysis and Calculation of the Optical Thin Film Density Uniformity

In accordance with the above results of TiO_2 film, does the wavelength shift possess a simple relation to the related packing density? This will be shown by the following experiments.

The calculation method is similar to equations (2)~(4). When the thin film are exposed to a humid atmosphere, the wavelength shift of the thin film is related to its own microstructure. Because the film index n in equations (2)~(4) is measured in a humid atmosphere, the refractive index n_v is a function of relative humidity, with

$$1.0 \leq n_v(\text{r. h.}) \leq 1.33 \tag{5}$$

In the experiment, the amorphous TiO_2 thin films, deposited by IAD using different deposition parameters, are investigated, and both of their indices are 2.390 measured in vacuum at wavelength of 550nm. If giving a relative bulk index value of 2.50 and using equation (2), the relative packing densities are all 0.9267. When exposing the thin films to humid atmosphere, the measured drifted indices are 2.390 and 2.399, respectively. It is reasonable to assume the value of n_{v2} as 1.33 when the water molecule penetrates the voids in the film. If

relative packing density is still calculated by equation (2), both of their relative packing densities are 0.9060 and 0.9137, respectively. This result shows that they have a different relative packing density in vacuum and in humid atmosphere. The reason for this is that all the voids are not completely filled with water molecules. This can be explained by uniformity of the microstructure. It is difficult to calculate the packing density by the above equations because the bulk index value is assumed, and the water molecules cannot penetrate into some of the mocro-voids. Thus, it is necessary to analyze and induce a factor relative to water sorption by means of equations (2)~(4). Rearranging equations (2)~(4) to

$$n_b' = (n_i - n_{vi} + p n_{vi})/p_w \tag{6}$$

$$n_b'^2 = (2n_i^2 - 2nv_i^2 + p_w n_{vi}^2 n_i^2 + 2p_w n_{vi}^2)/(p_w n_i^2 + 2p_w - n_i^2 + n_{vi}^2) \tag{7}$$

$$n_b'^2 = [(1+p_w) n_{vi}^2 n_i^2 - (1-p_w) n_{vi}^4]/[(1+p_w) n_{vi}^2 - (1-p_w) n_i^2] \tag{8}$$

where n_b' is the index of a part of film which has not absorbed water yet; $i = 1$, n_1 and n_{v1} are respectively the indices of the thin film and the void in vacuum; $i = 2$, n_2 and n_{v2} are the indices of the thin film and void in a humid atmosphere respectively, and p_w is defined as density uniformity coefficient related to water. For a more accurate calculation of the density uniformity coefficient, the index of the film in a humid atmosphere should be measured after boiling the thin film in water or completing the humidity test. Since a part of film index is a constant value both in vacuum and humid atmosphere, equations (6)~(8) can be respectively expressed as

$$p_w = 1 - \frac{n_2 - n_1}{n_{v2} - n_{v1}} \tag{9}$$

$$p_w = \frac{4(n_{v1}^2 n_2^2 - n_{v2}^2 n_1^2) - (4 + n_{v1}^2 n_{v2}^2)(n_1^2 - n_2^2)}{(n_{v1}^2 - n_{v2}^2)(4 + n_1^2 n_2^2 + 2n_1^2 + 2n_2^2)} + \frac{4 + n_1^2 n_2^2}{4 + n_1^2 n_2^2 + 2n_1^2 + 2n_2^2} \tag{10}$$

$$p_w = \frac{A_2 - \sqrt{A_2^2 - A_1 A_3}}{A_1} \tag{11}$$

where $A_1 = (n_{v1}^2 - n_{v2}^2)(n_{v2}^2 + n_2^2)(n_1^2 + n_{v1}^2)$,

$A_2 = (n_{v1}^2 + n_{v2}^2)(n_{v1}^2 n_2^2 - n_1^2 n_{v2}^2)$,

$A_3 = (n_{v1}^2 - n_{v2}^2)(n_{v2}^2 - n_2^2)(n_1^2 - n_{v1}^2)$.

4 Experimental, Results and Discussion

Shincron SX-1100 ion-beam assisted deposition (IAD) system with a diameter of 120 mm radio frequency type ion source was used for this experiment. A schematic alignment of the chamber is illustrated in Fig. 1. The substrate is BK7, about 30 mm in diameter and 1 mm thick. The physical and optical thicknesses are controlled with a quartz crystal monitor and the optical monitor of reflectance mode, respectively. The calculation of index in vacuum and air is by means of reflective optical monitor. During the depositon, RF ion source provided an energetic ion beam of oxygen except the EB deposition. The substrates were pre-cleaned with oxygen ions of 500eV for 2 minutes before film deposition. As the calculation model, the TiO_2 thin film is adopted. Its starting material is Ti_3O_5 and the process parameters are summarized

in Table 1.

Fig. 1 Schematic diagram of the ion-beam assisted deposition apparatus

Table 1 The process parameters of TiO_2 single layer films deposited by conventional EB and IAD methods

Annotations in Tab. 2 & Fig. 2	a	*b*, *c*	*d*, *e*	*f*, *g*	*h*	*i*, *j*
Starting material:	Ti_3O_5					
Ultimate pressure (Pa):	$\leq 5.0\times10^{-4}$					
Substrate temperature (℃):	260	*b*, *d*, *f*, *h* > 150 *c*, *e*, *g*, *i*, *j* < 150				
O_2 partial pressure (Pa):	$(1.3\sim2.0)\times10^{-2}$					
Deposition rate (nm/s):	0.6	0.1				
Ion energy (eV):	…	500				
Ion current density ($\mu A/cm^2$)	…	20	20	10, 20	20	20
Ratio of Ar: O_2:	…	Ar only	1∶1	1∶2	1∶5	O_2 only

In case of the relative bulk index of 2.50, the experimental results of TiO_2 thin film with indices n_1 and n_2, deposited by conventional EB and IAD using different parameters, are insert in equations (2)~(4) and (9)~(11). The results of relative packing density p and the density uniformity coefficient p_w are listed in Table 2. The annotations on the n_1 column signify the respective cross-sectional microstructures, taken by scanning electron microscope (SEM), are shown in Fig. 2.

Vaopr deposited films have been found to have a columnar microstructure, shown in Fig. 2(a), resulting from a low atom mobility. The presence of ions has been found to increase the atom mobility, accelerate the nucleation process, thereby increasing the packing density of the films. For proving the importance of density uniformity, a mixture of oxygen atoms and argon is introduced to the bombardment[8][10]. Since the ion penetration leads to different void sizes in the film, the packing density is dependence on the void size according to equation (1). In

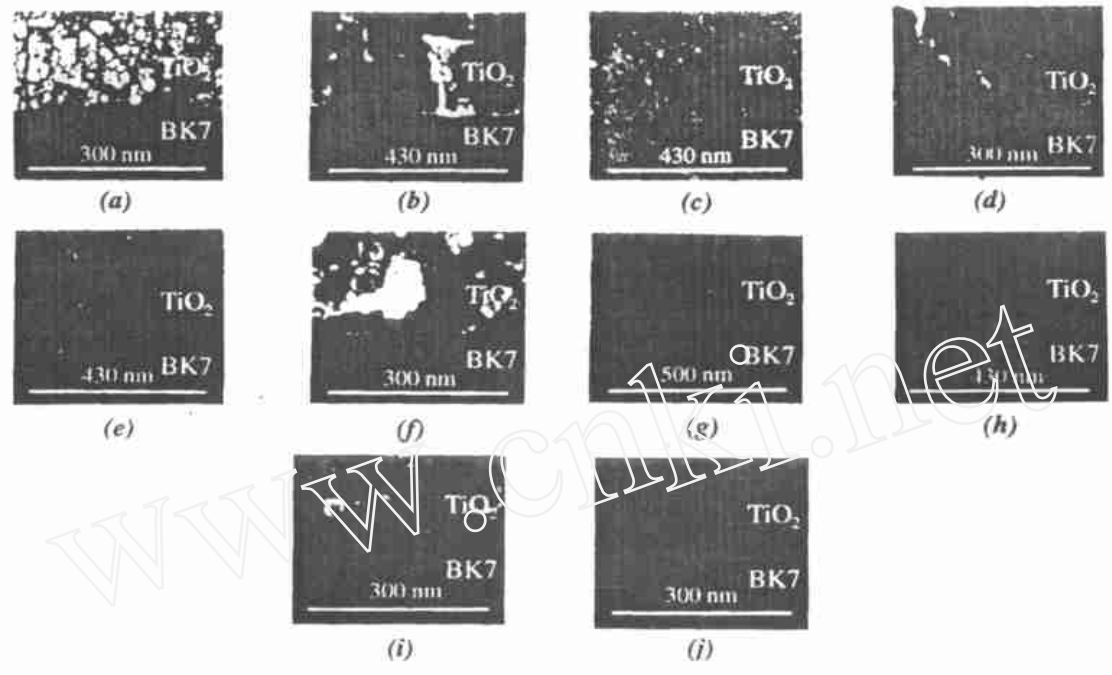

Fig. 2 Cross-sectional morphologies of TiO_2 film deposited by IAD (except Fig. 2(*a*) deposited by EB) with different process parameters shown in Table 2.

Table 2 Calculation of relative packing densities and density uniformity coefficients related to water sorption of TiO_2 thin film, deposited by conventional EB (first row) and IAD (after first row) methods using different process parameters

		p			p_w		
n_1	n_2	Eqn. 2	Eqn. 3	Eqn. 4	Eqn. 9	Eqn. 10	Eqn. 11
2.180[a]	2.286	0.7867	0.8733	0.9008	0.6788	0.8573	0.9198
2.216	2.302	0.8107	0.8893	0.9137	0.7394	0.8867	0.9367
2.251	2.343	0.8340	0.9043	0.9257	0.7212	0.8826	0.9354
2.300	2.322	0.8667	0.9248	0.9419	0.9333	0.9723	0.9846
2.309	2.368	0.8727	0.9284	0.9447	0.8212	0.9273	0.9603
2.318[b]	2.356	0.8787	0.9320	0.9476	0.8849	0.9531	0.9743
2.322[c]	2.322	0.8813	0.9337	0.9488	1.0000	1.0000	1.0000
2.342	2.411	0.8947	0.9416	0.9551	0.7909	0.9175	0.9557
2.349[d]	2.380	0.8993	0.9444	0.9572	0.9061	0.9626	0.9797
2.351[e]	2.351	0.9007	0.9451	0.9578	1.0000	1.0000	1.0000
2.360	2.405	0.9067	0.9486	0.9606	0.8636	0.9465	0.9712
2.363[f]	2.402	0.9087	0.9498	0.9615	0.8818	0.9536	0.9750
2.390[g]	2.390	0.9267	0.9601	0.9695	1.0000	1.0000	1.0000
2.390	2.399	0.9267	0.9601	0.9605	0.9727	0.9894	0.9943
2.399	2.492	0.9327	0.9635	0.9721	0.7182	0.8950	0.9451
2.436[h]	2.436	0.9573	0.9773	0.9826	1.0000	1.0000	1.0000
2.460[i]	2.500	0.9733	0.9859	0.9893	0.8788	0.9561	0.9771
2.495[j]	2.495	0.9967	0.9983	0.9987	1.0000	1.0000	1.0000

Table 2, the relative packing density of the item with annotation from *a* to *j* increases with the increase of their indices. The density uniformity coefficients, however, are not dependent on their indices. From their microstructures shown in Figure 2, the cross-sectional morphologies of 2(*c*), 2(*e*), 2(*g*), 2(*h*), and 2(*j*) show amorphous-like, and their density uniformity coefficients equal 1.0. Other morphologies in Figure 2 have a columnar structure, and their density uniformity coefficients are less than 1.0 because water vapor penetrates into the voids between the columns. Thus, the density uniformity coefficient is dependent on the number and the size of voids. If the size of the voids is less than that of water molecules, the water penetration phenomenon will not occur. Since the resolution power of SEM is not enough to reveal the micrstructure down to a scale of several nanometers, it is difficult to distinguish the structural differences among Figures 2(*c*), 2(*e*), 2(*g*), 2(*h*), and 2(*j*). This is why the film, with an index less than that of $p_w < 1.0$, can obtain a density uniformity coefficient equal to 1.0.

5 Conclusions

Table 2 shows the character that the relative packing density of the thin film depends on its index and the water sorption depends on the density uniformity coefficient. Permeation of water is caused by some microstructures in film, and it depends on the density uniformity coefficient relative to water and not on the packing density in some cases. Since there is a relationship between structure density and microstructural property, the morphology of thin film strongly affects both the packing density and density uniformity coefficient. This is especially true for the relative packing density and density uniformity coefficient of the thin films, for roughness, water sorption and diffusion behavior, optical behavior such as drift of index, and for mechanical properties such as relatively high stresses.

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